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COMMENT ON "DETECTION OF MULTIPLY DEUTERATED METHANE IN THE ATMOSPHERE"

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Abstract. It has recently been reported [Mroz et al., 1989] that the abundance of mass-20 isotopes of methane (CH_4), which correspond to either of the highly deuterated forms $^{12}CD_4$ or $^{13}CHD_3$, is some 500 times that expected based on the statistical combination of H, D, ^{12}C, and ^{13}C and observed CH_4 amounts. These authors then suggested that it is possible that the enhanced concentration of these species is due to their longer lifetimes than that of CH_4 itself because of their slower rate of loss by reaction with the hydroxyl radical (OH). We have tested this hypothesis with a two-dimensional atmospheric chemical-dynamical model and found that no large enhancements of $^{13}CHD_3$ and $^{12}CD_4$ can result in this way; in the troposphere enhancement factors of between 4 and 5 and between 7 and 8, respectively, were found, with enhancements becoming only slightly larger (14 and 25, respectively) in the stratosphere. The factor of 500 enhancement reported by Mroz et al. must have other origins.

Introduction

Recently, Mroz et al. [1989] reported that the abundance of mass-20 isotopomers of CH_4, which correspond to the molecules $^{13}CHD_3$ and $^{12}CD_4$ (which are used as tracers of atmospheric transport), is at least 500 times that expected based on the statistical abundances of hydrogen (H), deuterium (D), and ^{12}C and ^{13}C.

They were not able to account for this anomaly, but suggested that some enhancement in the concentrations of $^{13}CHD_3$ and $^{12}CD_4$ could arise from the fact that their chemical removal from the atmosphere should be appreciably slower than that of unsubstituted CH_4 because the rate of chemical reaction of OH is much slower for the former than the latter [Gordan and Mulac, 1975]. They also noted that it might not be possible to estimate the lifetime of these isotopomers of CH_4 because of the importance of transport to the stratosphere as a CH_4 loss process. Finally, they suggested that then enhanced lifetimes of multiply deuterated methanes could lead to enhanced production of deuterated water vapor in the stratosphere.

We have tested these hypotheses using a two-dimensional (2-D) atmospheric chemical-dynamical model covering the troposphere, stratosphere, and lower mesosphere. The purpose of this comment is to present the results of 2-D model calculations on $^{13}CHD_3$ and $^{12}CD_4$.

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Model Calculations

Our approach to testing these hypotheses is to use an established 2-D atmospheric model to provide for transport and chemical reactions of trace constituents. Applications of this model to ozone [Jackman et al., 1989a] and nitrogen oxides [Douglass et al., 1989] in the stratosphere have previously been made; the model has been extensively compared with other 2-D models in a recent conference proceedings [Jackman et al., 1989b].

For studying the distribution of isotopically substitued methanes we have assumed that they are emitted into the atmosphere from the ground with a flux proportional to that of CH_4 based on the statistical abundances of H, D, ^{12}C, and ^{13}C. A CH_4 flux of $9.75x10^{10}cm^{-2}s^{-1}$(corresponding to a total global flux of $417x10^{12}gy^{-1}$, which is close to the value of $500x10^{12}gy^{-1}$ cited by Mroz et al. [1989]) was found to give a tropospheric CH_4 mixing ratio slightly in excess of 1.6 parts per million by volume (ppmv). The flux ratios $^{13}CHD_3/CH_4$ and $^{12}CD_4/CH_4$ are $1.51x10^{-13}$ and $5.06x10^{-16}$, respectively, and were calculated based on the isotope ratios given in table 2 of the paper by Kaye [1987].

The atmospheric lifetimes of CH_4 and CH_3CCl_3 have been calculated with this model. That calculated for CH_4 was 9.9 years, while that for methyl chloroform (CH_3CCl_3), known from observations, was 6.1 years. A recent compilation [Watson et al., 1988] showed lifetimes of aproximately 10 and between six and eight years for these two species, respectively.

As suggested by Mroz et al. [1989] we assume the reaction rates of OH with $^{13}CHD_3$ and $^{12}CD_4$ are a factor of 0.2 and 0.1, respectively, times that of OH with CH_4. These ratios are taken from the measurements of Gordon and Mulac [1975], which were made at 416K and may not be entirely accurate for atmospheric temperatures. We assume similar factors for the reaction of Cl with CH_4 because, like the reaction with OH, it is a hydrogen atom abstraction reaction with a large activation energy and similar mass factors. We assume no isotope effect for the reaction of electronically excited oxygen atoms (O^1D), however, because this is an insertion reaction with little or no activation energy. The chemical origins of isotope effects as applied here are described more fully by Kaye [1987].

Because the isotopically substituted methanes were added to the results of a base state of the model and their lifetimes are several decades long (see below), the model was integrated for a long period of time (320 years).

Results and Discussion

The major results from these calculations are presented in Figures 1 and 2, in which the ratios of the calculated

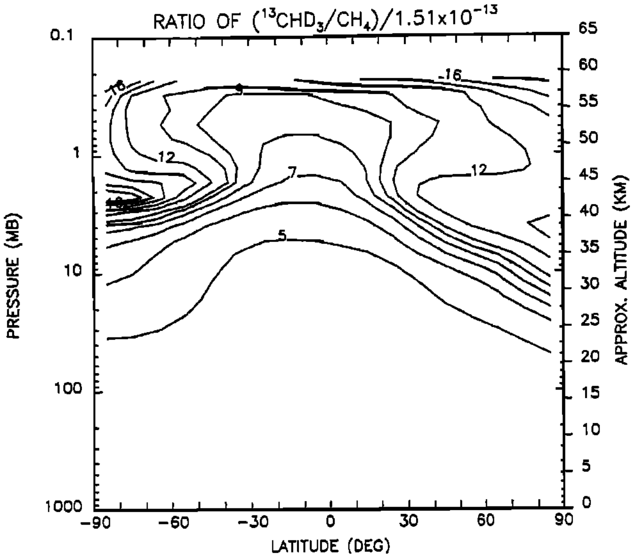

Fig. 1. Plot showing ratio of zonal mean distribution of $^{13}CHD_3$ to that expected based on calculated distribution of CH_4 and a statistical ratio of $^{13}CHD_3$ and CH_4.

two-dimensional distributions of $^{13}CHD_3$ (Figure 1) and $^{12}CD_4$ (Figure 2) to those expected based on statistical isotopic abundance are shown. One can see that in the troposphere and lower stratosphere a ratio of between 4 and 5 is found for $^{13}CHD_3$, while one between 7 and 8 is found for $^{12}CD_4$. Thus, nothing close to the factor of 500 enhancement measured by Mroz et al. [1989] is expected. The latitude and altitude dependence of these enhancements is also seen. For both $^{13}CHD_3$ and $^{12}CD_4$, the enhancement is largest at high altitudes and high latitudes, while it is lowest in regions of upwelling in the tropics. This may be easily understood in terms of the diabatic circulation which is responsible for much of the vertical transport

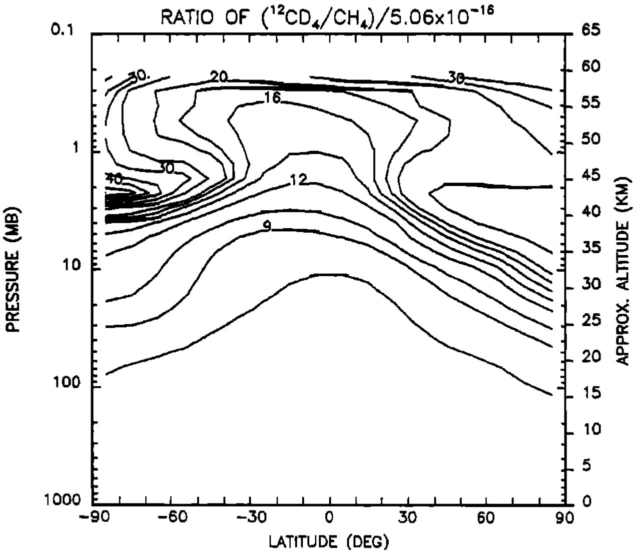

Fig. 2. Plot showing ratio of zonal mean distribution of $^{12}CD_4$ to that expected based on calculated distribution of CH_4 and a statistical ratio of $^{12}CD_4$ and CH_4.

in the atmosphere. The largest enhancements calculated for the stratosphere are 14 for $^{13}CHD_3$ and 25 for $^{12}CD_4$. Since the statistical D/H ratio is so small (approximately 0.00015), these enhancements are not sufficiently large for multiply deuterated methanes to be an important source of deuterated water (HDO) in the upper stratosphere.

Finally, we have calculated the chemical lifetimes of $^{13}CHD_3$ and $^{12}CD_4$ in the atmosphere using the results of this 2-D simulation and found values of 45 and 82 years, respectively. These are somewhat smaller than the values estimated by Mroz et al. [1989] of 55 and 110 years based solely on the reaction with OH as a loss process.

These calculations show that the large enhancements in mass 20 isotopes of CH_4 observed by Mroz et al. [1989] cannot be strictly lifetime effects associated with the slower removal by reaction with OH. Only at most a factor of 5 enhancement can be explained (the reduced abundance of $^{12}CD_4$ relative to that of $^{13}CHD_3$ suggests that nearly all of the mass 20 signal should arise from $^{13}CHD_3$) in this way. The remaining factor of 100 must arise from a highly non-statistical distribution of sources of isotopically substituted CH_4, which could be either natural or anthropogenic.

References

Douglass, A. R., C. H. Jackman, and R. S. Stolarski, Comparison of model results transporting the odd nitrogen family with results transporting separate odd nitrogen species, *J. Geophys. Res., 94*, 9862-9872, 1989.

Gordon, S., and W. A. Mulac, Reaction of OH($X^2\pi$) radical produced by pulse radiolysis of water vapor, *Int. J. Chem. Kin. 7 (Symp. 1)*, 289-299, 1975.

Jackman, C. H., A. R. Douglass, P. D. Guthrie, and R. S. Stolarski, The sensitivity of total ozone and ozone perturbation scenarios in a two-dimensional model due to dynamical inputs, *J. Geophys. Res., 94*, 9873-9887, 1989a.

Jackman, C. H., R. K. Seals, Jr., and M. J. Prather, Two-Dimensional Intercomparison of Stratospheric Models, *NASA Conference Publication 3042*, NASA, Washington, D.C., 1989b.

Kaye, J. A., Mechanisms and observations for isotope fractionation of molecular species in planetary atmospheres, *Rev. Geophys., 25*, 1609-1658, 1987.

Mroz, E. J., M. Alei, J. H. Cappis, P. R. Guthals, A. S. Mason, and D. J. Rokop, Detection of multiply deuterated methane in the atmosphere, *Geophys. Res. Lett.*, 16, 677-678, 1989.

Watson, R. T., M. J. Prather, and M. J. Kurylo, eds., Present State of Knowledge of the Upper Atmosphere 1988: An Assessment Report, *NASA Reference Publication 1208*, NASA, Washington, D. C., 1988.

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